Pergamon

PII: S0277-5387(96)00460-3

Polyhedron Vol. 16, No. 11, pp. 1889–1893, 1997

0277-5387/97 $17.00+0.00

Crystal and molecular structures of bis[2-(2-benzoxazolyl)phenol-*N*]dichloropalladium(II)

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(Received 4 June 1996; accepted 16 September 1996)

Abstract—The crystal and molecular structure of bis[2-(2-benzoxazolyl)phenol-*N*]dichloropalladium(II), was determined by the single-crystal X-ray diffraction. The palladium atom is at the symmetry centre in a square-planar geometry, where two 2-(2-benzoxazolyl)phenol (Hbxp) molecules are coordinated with their N atoms as unidentate ligands in the *trans* position. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: palladium(II) complex; 2-(2-benzoxazolyl)phenol; synthesis; X-ray analysis.

2-(2-Benzoxazolyl)phenol (Hbxp) has been known as an analytical chelating reagent for many bivalent metals such as zinc, cadmium and copper. Of these, the structures of the copper(II) and cadmium(II) complexes have already been determined by single-crystal X-ray diffraction [1]. As a result of ongoing work on the synthesis of the complexes of Hbxp, Furuhashi and workers have reported the synthesis and X-ray structure of the iron(III) [2], platinum(II) [3] and platinum(V) [4] complexes. In the iron(III) complex, Hbxp acts as a uninegative ion, bxp$^-$, coordinating to the metal atom through its benzoxazolyl-N and phenolato-O atoms and forming a chelate ring as reported in the cases of copper(II), cadmium(II) and palladium(II) [1]. In the case of platinum(V), Hbxp not only coordinates as a uninegative bxp$^-$, but the crystal contains neutral, uncoordinating Hbxp molecules. In the platinum(II) complex, Hbxp acts as a unidentate non-charged Hbxp ligand coordinating through its benzoxazolyl-N atom. Owing to a twisting of the planes of the two Hbxp ligands in the *cis* position of the square-planar Pt^{II}, two kinds of optical isomers could be obtained simultaneously. We have now obtained a new palladium(II) complex of Hbxp, $PdCl_2(Hbxp)_2$, in crystal form, which is different from that reported by Urdy [5]. The crystal and molecular structures were determined by the single-crystal X-ray diffraction technique.

EXPERIMENTAL

Synthesis of bis[2-(2-*benzoxazolyl*)*phenol*]*dichloropalladium*(*II*)

A solution of Hbxp (0.55 g) in n-propanol (150 cm^3) was added to a solution of *trans*-bis(benzonitrile)dichloropalladium [6] (0.5 g) in n-propanol (50 cm^3). The mixture was left standing for about 20 days. A light precipitate was removed by shaking and decanting, fresh n-propanol was added and this action was repeated many times until the light precipitate was completely removed, leaving a heavy precipitate. The residual orange–yellow crystals were dried on a porous sheet and in a desiccator over silica gel. Found: C, 52.1; H, 3.1; N, 4.6. Calc. for $C_{26}H_{18}N_2O_4Cl_2Pd$: C, 52.1; H, 3.1; N, 4.7%.

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Table 1. Crystal data and refinement details

Chemical formula	$C_{26}H_{18}N_2O_4Cl_2Pd$
Formula weight	599.77
Unit-cell dimensions	a = 11.718(4) Å b = 12.929(4) Å c = 17.225(6) Å β = 98.95(3)°
Volume of unit cell	2398(1) $Å^3$
Crystal system	Monoclinic
Space group	$P2_1/a$
Z value	4
Densities	
D_m	1.60 g cm^{-3}
D_x	1.63 g cm^{-3}
Total reflections	7002
R_{int}	0.07
Structure solution	SHELXS-86
Structure refinement	SHELXL-93
Least squares refinement	Full matrix
Function minimized	$\Sigma\,[w(\lvert F_0\rvert - \lvert F_c\rvert)^2]$
Weight method	$w = (\sigma_c{}^2 + (0.02\,\lvert F_0\rvert)^2)^{-1}$
$F(000)$	1199
Reflections used in L. S.	3008
Data reduction cut-off	$\lvert F_0\rvert > 3\sigma(\lvert F_0\rvert)$
R	0.055
R_w	0.063

Crystal structure determination

The crystal used for the X-ray analysis was chosen from the synthesized product, then shaped into a $0.40 \times 0.40 \times 0.45$ mm^3 block. The crystallographic data and some experimental conditions used to obtain the intensity data are given in Table 1. The reflections were collected on a Rigaku AFC-5S automated four-circle diffractometer with the graphite-monochromated Mo-K_α radiation ($\lambda = 0.7107$ Å) [scan speed: 4° min^{-1} (θ)] at the University of Tokyo using the ω–θ scan technique.

Structure determination

The structure of the complex was solved using Patterson and Fourier syntheses. The positional and thermal parameters were refined by the full-matrix, least-squares procedure. At the final stage, all the non-hydrogen atoms were refined anisotropically. All the calculations were carried out with the SHELXS-86 [7] and the SHELXL-93 [8] programs for crystal structure determination.

RESULTS AND DISCUSSION

Selected bond lengths and bond angles for the title complex are given in Tables 2 and 3. Although there are two crystallographically independent complex molecules, each of which is positioned at the centre of symmetry, they are almost identical so only one is shown in Fig. 1, which shows the palladium complex as viewed from above the coordination plane. The complex molecules have the *trans* configuration with two Cl atoms and two Hbxp molecules, which act as neutral unidentate ligands through the N atoms of the oxazolyl rings. The Pd—Cl and Pd—N distances are 2.299 and 2.002 Å, respectively. These values are a little shorter than the values expected from the sum of Shannon's ionic radii [9] (Pd—N = 2.10;

Table 2. Intramolecular bond lengths (Å)

Pd(1)—Cl(1)	2.299(3)	Pd(2)—Cl(2)	2.298(3)
Pd(1)—N(1)	2.002(9)	Pd(2)—N(2)	2.026(8)
O(11)—C(101)	1.341(14)	O(21)—C(201)	1.367(15)
O(12)—C(107)	1.358(14)	N(2)—C(207)	1.272(13)
O(12)—C(108)	1.357(14)	N(2)—C(213)	1.399(15)
N(1)—C(107)	1.313(14)	O(22)—C(207)	1.385(13)
N(1)—C(113)	1.421(14)	O(22)—C(208)	1.370(14)
C(101)—C(102)	1.368(17)	C(201)—C(202)	1.374(19)
C(101)—C(106)	1.408(16)	C(201)—C(206)	1.379(16)
C(102)—C(103)	1.402(18)	C(202)—C(203)	1.37(3)
C(103)—C(104)	1.32(2)	C(203)—C(204)	1.37(3)
C(104)—C(105)	1.37(3)	C(204)—C(205)	1.39(2)
C(105)—C(106)	1.372(17)	C(205)—C(206)	1.384(18)
C(106)—C(107)	1.477(18)	C(206)—C(207)	1.492(17)
C(108)—C(109)	1.417(18)	C(208)—C(209)	1.361(17)
C(108)—C(113)	1.379(16)	C(208)—C(213)	1.371(16)
C(109)—C(110)	1.35(3)	C(209)—C(210)	1.391(19)
C(110)—C(111)	1.39(3)	C(210)—C(211)	1.43(2)
C(111)—C(112)	1.41(2)	C(211)—C(212)	1.377(18)
C(112)—C(113)	1.361(16)	C(212)—C(213)	1.382(18)

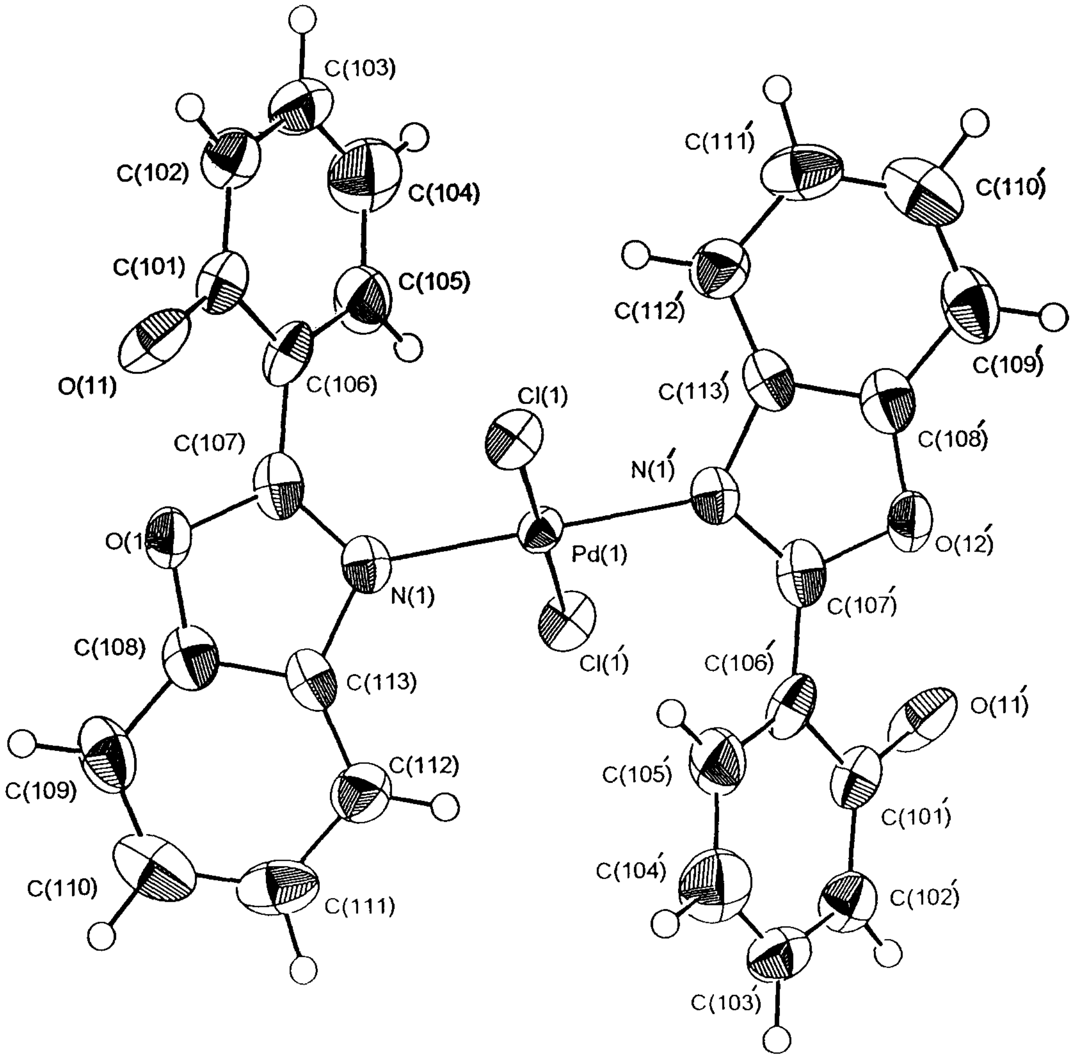

Fig. 1. The structure of one molecule of the complex.

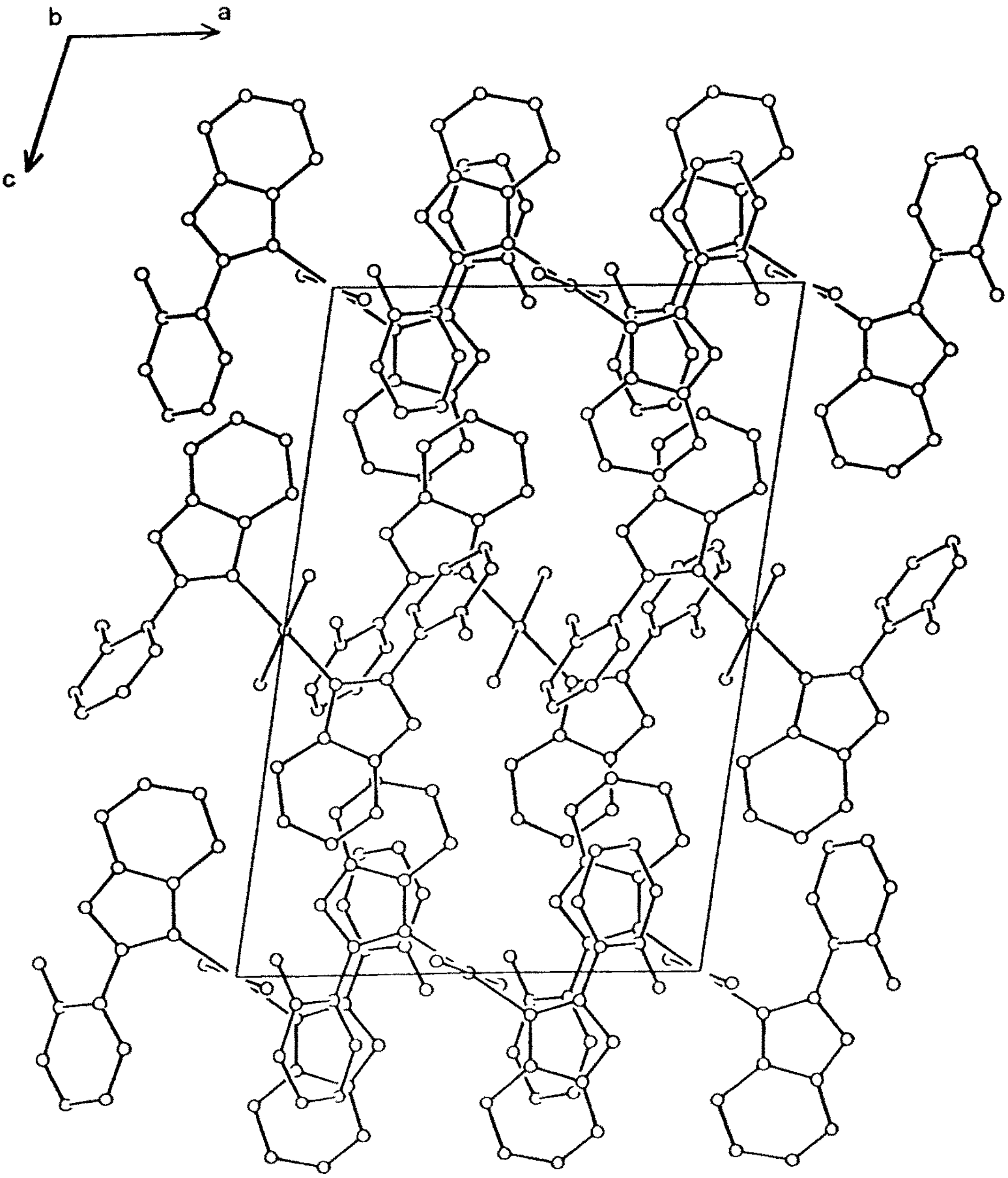

Fig. 2. Projection of the unit cell along the *b*-axis.

Table 3. Intramolecular bond angles (°)

Cl(1)—Pd(1)—N(1)	89.4(3)	Cl(2)—Pd(2)—N(2)	89.0(3)
Pd(1)—N(1)—C(107)	127.7(8)	Pd(2)—N(2)—C(207)	125.2(8)
Pd(1)—N(1)—C(113)	126.7(7)	Pd(2)—N(2)—C(213)	127.1(7)
C(101)—C(102)—C(103)	118.6(11)	C(201)—C(202)—C(203)	119.6(13)
C(102)—C(103)—C(104)	120.7(13)	C(202)—C(203)—C(204)	120.1(14)
C(103)—C(104)—C(105)	122.3(14)	C(203)—C(204)—C(205)	122.3(14)
C(104)—C(105)—C(106)	118.6(12)	C(204)—C(205)—C(206)	116.0(13)
C(101)—C(106)—C(105)	120.2(12)	C(201)—C(206)—C(205)	122.4(12)
C(102)—C(101)—C(106)	119.3(11)	C(202)—C(201)—C(206)	119.4(11)
O(11)—C(101)—C(102)	123.0(10)	O(21)—C(201)—C(202)	121.2(10)
O(11)—C(101)—C(106)	117.7(11)	O(21)—C(201)—C(206)	119.4(11)
C(101)—C(106)—C(107)	119.9(10)	C(201)—C(206)—C(207)	121.5(11)
C(105)—C(106)—C(107)	119.9(10)	C(205)—C(206)—C(207)	116.1(11)
N(1)—C(107)—C(106)	127.1(10)	N(2)—C(207)—C(206)	127.8(10)
O(12)—C(107)—C(106)	118.9(10)	O(22)—C(207)—C(206)	119.0(9)
C(107)—O(12)—C(108)	104.2(9)	C(207)—O(22)—C(208)	103.8(8)
O(12)—C(108)—C(113)	110.8(10)	O(22)—C(208)—C(213)	109.3(10)
N(1)—C(113)—C(108)	105.3(9)	N(2)—C(213)—C(208)	106.3(10)
C(107)—N(1)—C(113)	105.6(9)	C(207)—N(2)—C(213)	107.4(9)
O(12)—C(107)—N(1)	114.0(10)	O(22)—C(207)—N(2)	113.2(10)
O(12)—C(108)—C(109)	128.3(12)	O(22)—C(208)—C(209)	128.0(10)
N(1)—C(113)—C(112)	129.9(10)	N(2)—C(213)—C(212)	129.8(11)
C(109)—C(108)—C(113)	120.8(12)	C(209)—C(208)—C(213)	122.6(11)
C(108)—C(109)—C(110)	115.6(13)	C(208)—C(209)—C(210)	115.3(12)
C(109)—C(110)—C(111)	122.5(13)	C(209)—C(210)—C(211)	122.0(13)
C(110)—C(111)—C(112)	122.6(13)	C(210)—C(211)—C(212)	121.2(13)
C(111)—C(112)—C(113)	113.7(11)	C(211)—C(212)—C(213)	114.9(12)
C(108)—C(113)—C(112)	124.6(11)	C(208)—C(213)—C(212)	123.9(12)

Pd—Cl = 2.45 Å). The two phenol rings are also headed in opposite directions with a little twisting between the plane of the metal atom and the plane of the oxazolyl ring, the dihedral angle between the oxazoryl ring and the phenol ring being 128.90°. Thus, this palladium complex as a whole is in complete symmetry with the palladium atom at the symmetry centre of the complex molecule in a square-planar configuration. This is different from the palladium(II) complex reported by Urdy [5]. He obtained the complex formulated as $Pd(bxp)_2$, the ligand acting as a uninegative bidentate. We have synthesized the complex in a neutral medium which is different from Urdy's method, which used a basic medium.

A projection of the unit cell along the *b*-axis is shown in Fig. 2. The complex molecules are arranged in parallel and are laid along the *a*-axis.

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